

WHEREAS, We, Junji Momoda and Tadashi Hara, Japanese citizens,
both of us,
residing at the same address of c/o Tokuyama Corporation, 1-1, Mikage-cho,
Tokuyama-shi, Yamaguchi-ken, Japan, respectively,

, (hereafter referred to as Inventors), have invented certain new
and useful improvements in PHOTOCHROMIC CURABLE COMPOSITION

which was executed by us on ..February 18, 1999....., and filed in the
United States Patent and Trademark Office on ..N/A.....
under Serial No. ..N/A.....

WHEREAS, Tokuyama Corporation
a corporation of Japan, having a place of business at
1-1, Mikage-cho, Tokuyama-shi, Yamaguchi-ken, Japan
(hereafter referred to as Company), is desirous of acquiring the entire right,
title and interest in and to said invention and in and to any Letters Patent
that may be granted therefor in the United States and in any and all foreign
countries.

NOW THEREFORE, in consideration of the sum of One Dollar (\$1.00) to us in
hand paid, the receipt whereof is hereby acknowledged, and other valuable
considerations, the said Inventors have sold, assigned and transferred, and
by the presents do sell, assign and transfer unto said Company the full and
exclusive right to the said invention in the United States and its territorial
possessions and in all foreign countries and the entire right, title and
interest in and to any and all Letters Patent, which may be granted thereof
in the United States and its territorial possessions and in any and all foreign
countries and in and to any and all divisions, reissues, continuations and
extensions thereof.

We hereby authorize and request the Patent Office Officials in the United
States and in any and all foreign countries to issue any and all of said Letters
Patent, when granted, to said Company as the assignee of the entire right, title
and interest in and to the same, for the sole use and behoof of the said Company,
its successors and assigns.

FURTHER, We agree that we will communicate to said Company or its representa-
tives any facts known to us respecting said invention, and testify in any legal
proceedings, sign all lawful papers, execute all divisional, continuation,
substitution, renewal and reissue applications, execute all necessary assignment
papers to cause any and all of said Letters Patent to be issued to said Company,
make all rightful oaths and generally do everything possible to aid said Company,
its successors and assigns, to obtain and enforce proper protection for said
invention in the United States and in any and all foreign countries.

IN TESTIMONY WHEREOF, We have hereunto set our hands this ..18th..... day
ofFebruary....., 19 99

Signed in the presence of:

Witness: Nobuo Adachi

Witness: Shingo Matsui

Witness:

Witness:

Witness:

Witness:

Signed: Junji Momoda

Signed: Tadashi Hara

Signed:

Signed:

Signed:

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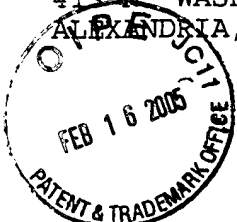
PTAS



100988409A

SPD. 507

SHERMAN AND SHALLOWAY
LEONARD W. SHERMAN
413 N. WASHINGTON STREET
ALEXANDRIA, VA 22314



UNITED STATES PATENT AND TRADEMARK OFFICE
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RECORDATION DATE: 03/02/1999

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BRIEF: ASSIGNMENT OF ASSIGNOR'S INTEREST (SEE DOCUMENT FOR DETAILS).

ASSIGNOR:
MOMODA, JUNJI

DOC DATE: 02/18/1999

ASSIGNOR:
HARA, TADASHI

DOC DATE: 02/18/1999

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SERIAL NUMBER: 09260005
PATENT NUMBER:

FILING DATE: 03/02/1999
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9819/0116 PAGE 2

PAULA MCCRAY, EXAMINER
ASSIGNMENT DIVISION
OFFICE OF PUBLIC RECORDS

03-19-1999

35 U.S.C. 101

SPO-567

Tab settings □ □ □ ▼



To the Honorable Commissioner of

100988409

, attached original documents or copy thereof.

1. Name of conveying party(ies):

Junji Momoda
Tadashi Hara

2. Name and address of receiving party(ies)

Name: Tokuyama Corporation

Internal Address: _____

Additional name(s) of conveying party(ies) attached? ☐ Yes ☒ No

3. Nature of conveyance:

☒ Assignment

Merger

☐ Security Agreement☐ Change of Name☐ Other _____

Execution Date: February 18, 1999

Street Address: 1-1, Mikage-cho, Tokuyama-shi
Yamaguchi-ken, Japan

City: _____ State: _____ ZIP: _____

Additional name(s) & address(es) attached? ☐ Yes ☒ No

4. Application number(s) or patent number(s):

If this document is being filed together with a new application, the execution date of the application is: Feb. 18, 1999

A. Patent Application No.(s)

B. Patent No.(s)

09/260005

Additional numbers attached? ☐ Yes ☒ No

5. Name and address of party to whom correspondence concerning document should be mailed:

Name: SHERMAN AND SHALLOWAY

Internal Address: _____

6. Total number of applications and patents involved: 1

7. Total fee (37 CFR 3.41).....\$ 40.00

☒ Enclosed☐ Authorized to be charged to deposit account

8. Deposit account number:

19-1980

(Attach duplicate copy of this page if paying by deposit account)

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9. Statement and signature.

To the best of my knowledge and belief, the foregoing information is true and correct and any attached copy is a true copy of the original document.

Leonard W. Sherman

Name of Person Signing

Signature

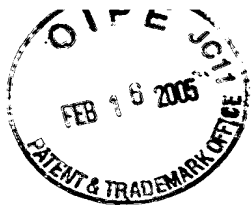
March 2, 1999

Date

Total number of pages including cover sheet, attachments, and document: 2

Chromene Compounds

No	Structure	Name	Molecular weight
1)		Spiro(norbornane-2,2'-[2H]benzo[h]chromene)	262
2)		Spiro(bicyclo[3.3.1]nonane-9,2'-[2H]benzo[h]chromene)	290
3)		7'-MethoxySpiro(bicyclo[3.3.1]nonane-9,2'-[2H]benzo[h]chromene)	320
4)		7'-MethoxySpiro(norbornane-2,2'-[2H]benzo[h]chromene)	292
5)		3,3-Bis(3-fluoro-4-methoxyphenyl)-6-morpholino-3H-benzo[f]chromene	515
6)		3,3-Bis(4-methoxyphenyl)-6-morpholino-3H-benzo[f]chromene	479
7)		3-(3-Trifluoromethyl-4-methoxyphenyl)-3-(methoxyphenyl)-6-thiomorpholino-3H-benzo[f]chromene	513



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

VERIFICATION OF TRANSLATION

Honorable Commissioner of Patent and Trademark
Washington, D.C. 20231

Sir:

KEIJI TOKIEDA residing at 2-20-204, Kaitori 2-chome, Tama-shi,
Tokyo, Japan, declares:

- (1) that he knows well both the Japanese and English languages;
- (2) that he translated the Japanese Patent Application No. 295835/99 from Japanese to English.
- (3) that the attached English translation is a true and correct translation of the above-identified Japanese Patent Application to the best of his knowledge and belief; and
- (4) that all statements made of his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 USC 1001, and that such false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: January 18, 2005

A handwritten signature in cursive script, appearing to read "Keiji Tokieda", written over a horizontal line.

Keiji Tokieda

Document Name: Patent Application

Reference Number: TKP9910182

To: Mr. Commissioner, Patent Office

International Patent Classification: G03C 1/73

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Claiming priority based on prior application:

Application No. 205165/99

Filing date: July 19, 1999

Indication of fee:

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List of Submitted Documents:

Material Name: Specification one copy

Material Name: Abstract one copy

Request for proof: requested

(Document Name) SPECIFICATION

(Title of the Invention) CURABLE COMPOSITION

(Scopes of Claims)

(Claim 1) A curable composition comprising:

a polymerizable monomer which, when homopolymerized, exhibits the L-scale Rockwell hardness of not larger than 40;

a bifunctional or polyfunctional polymerizable monomer which, when homopolymerized, exhibits the L-scale Rockwell hardness of not smaller than 60; and

a photochromic compound.

(Claim 2) A curable composition according to claim 1, wherein the photochromic compound has a molecular weight of not smaller than 540.

(Claim 3) A curable composition according to any one of claims 1 to 2, wherein the polymerizable monomer which, when homopolymerized, exhibits an L-scale Rockwell hardness of not larger than 40, is at least one kind of a polymerizable monomer selected from the group consisting of:

(I) an ethylenic monofunctional unsaturated monomer;

(II) a polyalkylene glycol polymerizable monomer or a polyalkylenethio glycol polymerizable monomer of which either a hydroxyl group or a mercapto group at the terminal is substituted by methacryloyloxy group, acryloyloxy group,

vinylbenzyloxy group, isopropenylbenzyloxy group, vinylbenzylcarbamoyl group, isopropenylbenzylcarbamoyl group or vinyloxy group, and of which other group is not substituted or is substituted by methacryloyloxy group, acryloyloxy group, and of which the other group is substituted by methacryloyl group, acryloyl group, alkyl group, aryl group, epoxy group, haloalkyl group, or oleyl group, or the other group is an unsubstituted polyalkylene glycol polymerizable monomer or polyalkylenethio glycol polymerizable monomer;

(III) long-chain (meth)acrylate;

(IV) a hydrocarbon chain (meth)acrylate having an unsaturated bond;

(V) an epoxy compound; and

(VI) a thioepoxy compound;

and the polymerizable monomer which, when homopolymerized, exhibits the L-scale Rockwell hardness of not smaller than 60 is:

(VII) a polyfunctional polymerizable monomer and/or

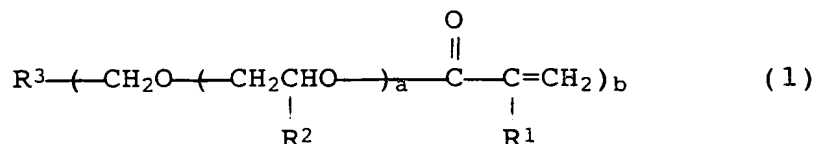
(VIII) a bifunctional polymerizable monomer.

(Claim 4) A curable composition according to claim 3, wherein

the polyalkylene glycol polymerizable monomer or the polyalkylenethio glycol polymerizable monomer (II) has a number-average molecular weight of from 200 to 2500;

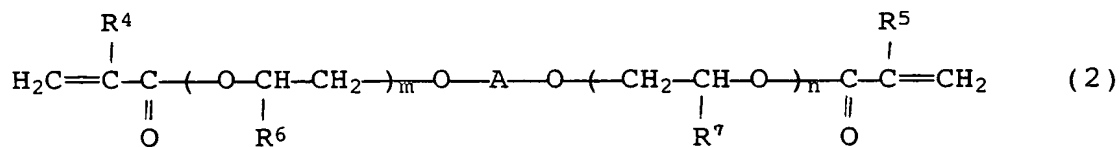
the long-chain alkyl (meth)acrylate (III) has a long-chain alkyl group containing 8 to 25 carbon atoms, or the hydrocarbon chain (meth)acrylate having an unsaturated bond (IV) has a hydrocarbon chain having 6 to 25 carbon atoms;

the polyfunctional polymerizable monomer (VI) is a polyfunctional polymerizable monomer represented by the following general formula (1),



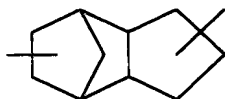
wherein R¹ and R² are, independently from each other, hydrogen atoms or alkyl groups having 1 to 2 carbon atoms, R³ is a trivalent to hexavalent organic residue, a is an integer of 0 to 20, and b is an integer of 3 to 6,

the bifunctional polymerizable monomer (VII) is a bifunctional polymerizable monomer represented by the following general formula (2),

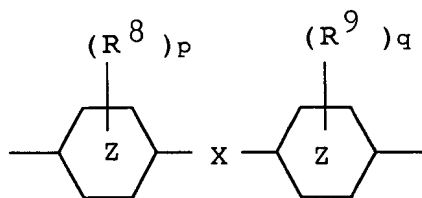


wherein R⁴ and R⁵ are, independently from each other, hydrogen atoms or methyl groups, R⁶ and R⁷ are independently from each other, hydrogen atoms or alkyl groups having 1 to 2 carbon atoms, A is a straight-

chain or branched-chain alkylene group, a substituted or unsubstituted phenylene group, a group represented by the following formula,



or a group represented by the following formula,



wherein R^8 and R^9 are, independently from each other, alkyl groups having 1 to 4 carbon atoms, chlorine atoms or bromine atoms, p and q are, independently from each other, integers of 0 to 4, a ring represented by the following formula

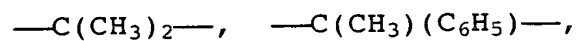
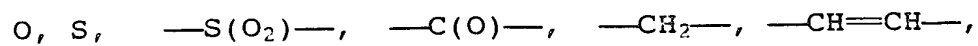


is a benzene ring or a cyclohexane ring, and when the ring represented by the following formula

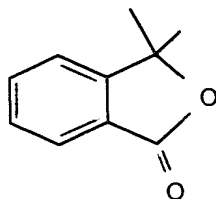


is a benzene ring, X is any one of the groups

represented by the following formulas



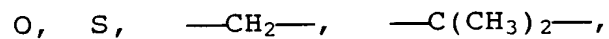
or a group represented by the following formula



and when the ring represented by the following formula

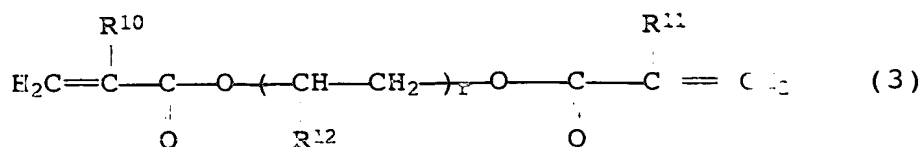


is a cyclohexane ring, X is any one of the groups represented by the following formulas



and m and n are an integer, respectively, and m + n is 1 to 10 in average,

or a bifunctional polymerizable monomer represented by the following general formula (3),



wherein R¹⁰ and R¹¹ are, independently from each other, hydrogen atoms or methyl groups, R¹² is a hydrogen atom or an alkyl group having 1 to 2 carbon atoms, and r is an integer of 1 to 10.

(Claim 5) A photochromic curable product obtained by curing the curable composition according to any one of claim 1 to claim 4.

(Detailed Description of the Invention)

(Industrial Field of Application)

The present invention relates to a novel photochromic cured product having excellent photochromic properties and matrix characteristics, and to a curable composition that yields the cured product.

(Prior Art)

Photochromism is a phenomenon that is drawing attention in these several years, and is a reversible action of a compound which quickly changes its color when it is irradiated with light containing ultraviolet rays such as sunlight or light of a fluorescent lamp and resumes its initial color when it is no longer irradiated with light but is placed in a dark place. The compound having this property is called photochromic compound. Various

compounds have so far been synthesized but no particular common nature is recognized in their structures.

The present inventors have forwarded the study concerning a series of photochromic compounds, have succeeded in synthesizing novel photochromic compounds such as fulgimide compounds, spirooxazine compounds and chromene compounds, have discovered that these compounds exhibit excellent photochromic properties, and have already proposed these compounds.

Through the study conducted by the present inventors up to now, it has been learned that the photochromic properties such as color density and fading rate of the photochromic compound are exhibited considerably sluggishly in the polymer as compared in a solution. This phenomenon becomes conspicuous particularly in a compound having photochromic molecules of large sizes. The development of this phenomenon is attributed to that free space in which the photochromic compound molecules are allowed to freely move is very limited in a matrix of polymer compared to that of in a solution.

In order to solve the above-mentioned problem, it can be contrived to make the base member soft by lowering the glass transition temperature of polymer of the matrix or to broaden free space in the matrix.

However, when a matrix having a low glass transition

temperature is simply used, hardness is lost bringing about a problem when the composition is used for the applications where a hardness is required, such as lenses. Further, when polymer having large free space is used as a matrix, the hardness of the polymer is usually much dependent upon the temperature. Even those that exhibit a relatively high hardness near room temperature show a rapidly dropped hardness at high temperatures (hereinafter also referred to as having a low heat resistance) and further show a decreased impact resistance.

U.S. Patent No. 5395566 teaches that the use of a polymerizable monomer having an epoxy group in combination with a photochromic compound, helps improve light resistance for the photochromic properties. With the combination of the radical polymerizable monomers described in the example of this specification, however, the physical properties of the base material, such as hardness and impact resistance are excellent, but in the case where the molecular size of the photochromic molecule is large, there are problems in that color density and fading rate are deteriorated.

The specification of U.S. Patent No. 5739243 teaches a system of a combination of a particular long-chain alkylene glycol dimethacrylate and a polyfunctional methacrylate having three or more radically polymerizable groups. From

this combination is obtained a cured product having improved color density and fading rate. However, this technology is for obtaining a matrix excellent in flexibility. With this combination as shown in working examples, the matrix has such problems as a decreased hardness, a decreased heat resistance and much optical distortion.

Further, the specification of U.S. Patent No. 5811503 discloses a system of a combination of a long-chain alkylene glycol dimethacrylate and a dimethacrylate.

Though improved color-developing rate and fading rate are exhibited, this combination, too, has such defects that the matrix exhibits a decreased hardness, a decreased heat resistance and much optical distortion.

The specification of PCT International Patent Application 97/03373 discloses a combination of a dimethacrylate with bisphenol A as a skeleton, a monofunctional styrene and a long-chain alkyl monofunctional methacrylate. However, this combination, too, has such defects that the matrix exhibits decreased hardness, a decreased heat resistance and much optical distortion.

As described above, no compound is ever satisfying both photochromic properties and matrix properties.
(Problems that the Invention is to Solve)

It is therefore an object of the present invention to provide a photochromic cured product exhibiting excellent photochromic properties such as a high color density and a large fading rate, and exhibiting excellent matrix characteristics such as a high hardness and a high heat resistance.

(Means of Solving the Problems)

The present invention was proposed in order to achieve the above object and was completed based on a knowledge that a cured product obtained by curing a curable composition obtained by mixing a photochromic compound with a combination of polymerizable monomers of particular hardnesses, exhibits excellent photochromic properties such as a high color density and a large fading rate, as well as excellent matrix properties in regard to hardness and heat resistance.

That is to say, the present invention is a curable composition characterized by comprising: a polymerizable monomer which, when homopolymerized, exhibits the L-scale Rockwell hardness of not larger than 40; a bifunctional or a polyfunctional polymerizable monomer which, when homopolymerized, exhibits the L-scale Rockwell hardness of not smaller than 60; and a photochromic compound.

The invention is further concerned with a photochromic cured product obtained by curing the above curable

composition.

(Working Examples)

A polymerizable monomer (hereinafter also simply referred to as "low-hardness monomer") which is used for the curable composition of the invention and which, when homopolymerized, exhibits an L-scale Rockwell hardness of not larger than 40, may be any known polymerizable monomer without any particular limitation provided a homopolymer obtained by the homopolymerization exhibits the L-scale Rockwell hardness of not larger than 40.

Here, the L-scale Rockwell hardness stands for a hardness measured in compliance with JIS-B7726. That is, the homopolymers of the monomers are measured to easily judge whether the above hardness condition is satisfied. Concretely speaking, as will be described in Examples appearing later, the monomer is polymerized to obtain a cured product having a thickness of 2 mm, which is, then, preserved in a room maintained at 25°C for one day and is, then, measured for its L-scale Rockwell hardness by using a Rockwell hardness meter.

As the monomers that can be favorably used as low-hardness monomers, there can be mentioned, for example, polymerizable monomers shown in the compounds (I) to (VI) described below, and a mixture of two or more kinds of polymerizable monomers optionally selected from these

polymerizable monomers:

(I) An ethylenic monofunctional unsaturated monomer (hereinafter also simply referred to as "low-hardness monomer 1").

(II) A polyalkylene glycol polymerizable monomer or polyalkylenethiol glycol polymerizable monomer (hereinafter also simply referred to as "low-hardness monomer 2") of which either a hydroxyl group at the terminal is substituted by methacryloyloxy group, acryloyloxy group, and of which the other group is substituted by methacryloyl group, acryloyl group, alkyl group, aryl group, epoxy group, haloalkyl group, or oleyl group, or the other group is an unsubstituted polyalkylene glycol polymerizable monomer or polyalkylenethio glycol polymerizable monomer;

(III) Long-chain alkyl (meth)acrylate (hereinafter simply referred to as "low-hardness monomer 3");

(IV) A hydrocarbon chain (meth)acrylate having an unsaturated bond (hereinafter simply referred to as a "low-hardness monomer 4");

(V) An epoxy compound (hereinafter simply referred to as a "low-hardness monomer 5"); and

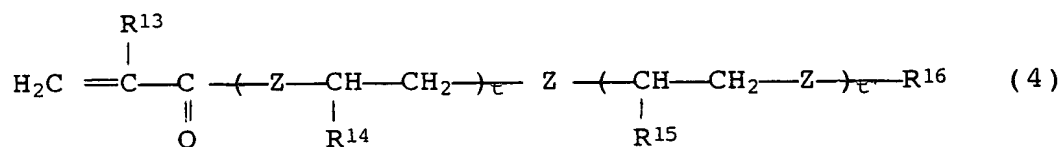
(VI) A thioepoxy compound (hereinafter simply referred to as a "low-hardness monomer 6").

Examples that can be favorably used as the low-hardness monomer 1 include vinyl acetate, vinyl caproate,

vinyl laurate, vinyl stearate and vinyl adipate.

The low-hardness monomer 2 is the one in which one of a hydroxyl group at a terminal of polyalkylene glycol or polyalkylenethiol glycol is substituted by methacryloyloxy group or acryloyloxy group, (i.e., a structure terminated by the dehydration-condensation with methacrylic acid or acrylic acid), and the other group is not substituted or is substituted by methacryloyl group, acryloyl group, alkyl group, aryl group, epoxy group, haloalkyl group, or oleyl group.

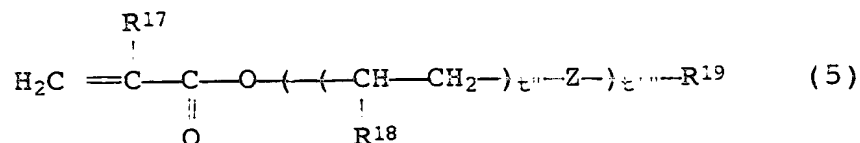
Generally, there is exemplified a monomer having a structure represented by the following general formula (4),



wherein R¹³, R¹⁴ and R¹⁵ are, independently from each other, hydrogen atoms or alkyl groups having 1 to 2 carbon atoms, R¹⁶ is a hydrogen atom, an alkyl group having 1 to 25 carbon atoms, an aryl group, an alkyl group having an epoxy group at the terminal, a haloalkyl group, an oleyl group) Z is an oxygen atom or a sulfur atom, a methacryloyl group, an acryloyl group, t is an integer of 4 to 70, and t' is an integer of 0 to 70,

or a monomer having a structure represented by the

following general formula (5),



wherein R¹⁷ and R¹⁸ are, independently from each other, hydrogen atoms or alkyl groups having 1 to 2 carbon atoms, R¹⁹ is a hydrogen atom, an alkyl group having 1 to 25 carbon atoms, an aryl group, an alkyl group having an epoxy group at the terminal, a haloalkyl group, an oleyl group, a methacryloyl group, or an acryloyl group, Z is an oxygen atom or a sulfur atom, t is an integer of 2 to 8 and t'' is an integer of 4 to 40.

The monomer represented by the above general formula is usually obtained in the form of a mixture of molecules having different molecular weights. Therefore, t and t'' representing the numbers of the alkylene oxide units in the above formulas (4) and (5), are expressed by average numbers of the units in the whole mixture. Here, t is generally from 4 to 70, in the case of being expressed in such a manner.

As the low-hardness monomer 2, the one having a number0average molecular weight (hereinafter simply referred to as "average molecular weight") of from 200 to 2500 is preferably used. The average molecular weight can

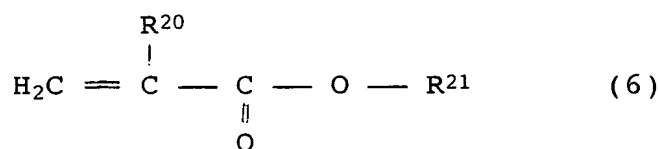
be determined by gel permeation chromatography (GPC) measurement.

Concrete examples of the low-hardness monomer 2 include a polyethylene glycol methacrylate having an average molecular weight of 526, a polyethylene glycol methacrylate having an average molecular weight of 360, a methyl ether polyethylene glycol methacrylate having an average molecular weight of 475, a methyl ether polyethylene glycol methacrylate having an average molecular weight of 1000, a polypropylene glycol methacrylate having an average molecular weight of 375, a polypropylene glycol methacrylate having an average molecular weight of 430, a polypropylene methacrylate having an average molecular weight of 622, a methyl ether polypropylene glycol methacrylate having an average molecular weight of 620, a polytetramethylene glycol methacrylate having an average molecular weight of 566, an octylphenyl ether polyethylene glycol methacrylate having an average molecular weight of 2034, a nonyl ether polyethylene glycol methacrylate having an average molecular weight of 610,

a polyethylene glycol dimethacrylate having an average molecular weight of 875, a polyethylene glycol dimethacrylate having an average molecular weight of 650, a

polytetramethylene glycol dimethacrylate having an average molecular weight of 1400, a polypropylene glycol dimethacrylate having an average molecular weight of 560, a methyl ether polyethylenethio glycol methacrylate having an average molecular weight of 640, and a perfluoroheptylethylene glycol methacrylate having an average molecular weight of 498.

The low-hardness monomer 3 is not particularly limited, so long as it is (meth)acrylate having a long-chain alkyl group, and for example, there can be used a long-chain alkyl (meth)acrylate represented by the following general formula (6),



wherein R^{20} is a hydrogen atom or a methyl group, and R^{21} is an alkyl group having 1 to 40 carbon atoms.

Among these long-chain alkyl (meth)acrylates, it is desired to use those in which, R^{21} is an alkyl group having 8 to 25 carbon atoms, from the standpoint of easy availability of the starting material. Concrete examples of such a long-chain alkyl (meth)acrylate include stearyl methacrylate and lauryl methacrylate.

As the low-hardness monomer 4, there can be used, without any particular limitation, any hydrocarbon chain

(meth)acrylate having an unsaturated bond in the hydrocarbon chain like a (meth)acrylate having 6 to 25 carbon atoms, such as oleyl methacrylate, nerol methacrylate, geraniol methacrylate, linalool methacrylate, and farnesol methacrylate.

As an epoxy compound, which is the low-hardness monomer 5, there can be exemplified (i) a reaction product of an alcoholic hydroxyl group-containing compound such as monohydric, dihydric or trihydric alcohol or a phenolic hydroxyl group-containing compound such as phenol or hydroquinone with epichlorohydrin, or (ii) a reaction product of a carboxylic acid such as benzoic acid or terephthalic acid with epichlorohydrin. Concrete examples of the above compound include ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, sorbitol polyglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidylether, and bisphenol A or propylene oxide adduct of a hydrogenated bisphenol A.

As a thioepoxy compound, which is the low-hardness monomer 6, there can be exemplified (i) a reaction product of a thiolic hydroxyl group-containing compound such as a monohydric, dihydric or trihydric thiol or a thiophenolic hydroxyl group containing compound such as thiophenol or a thiohydroquinone with a thioepichlorohydrin, or (ii) or a

reaction product of a thiocarboxylic acid such as thiobenzoic acid or thioterephthalic acid with a thioepichlorohydrin. Concrete examples of the above compound include ethylenethio glycol thioglycidyl ether, propylenethio glycol thioglycidyl ether, thioglycerol polythioglycidyl ether, thioglycerol polythioglycidyl ether, thiosorbitol thioglycidyl ether, polyethylenethio glycol thioglycidyl ether, polypropylenethio glycol thioglycidyl ether, and thiopropylene oxide adduct of a thiobisphenol A or a hydrogenated thiobisphenol A.

As the polymerizable monomer used in the curable composition of the present invention which, when homopolymerized, exhibits the L-scale Rockwell hardness of not smaller than 60 (hereinafter, simply referred to as "high-hardness monomers"), it is not particularly limited, so long as it is a polymerizable monomer having two or three or more polymerizable groups in the molecule where the L-scale Rockwell hardness of a homopolymer obtained by homopolymerization is not smaller than 60, and known polymerizable monomers can be used without any limitation. As the high-hardness monomers that can be favorably used, there can be mentioned polymerizable monomers, for example, shown in (VII) or (VIII) described below, and a mixture thereof. Confirmation method of the L-scale Rockwell hardness is the same as described in the above-described

low-hardness monomer:

(VII) a polyfunctional polymerizable monomer (hereinafter, simply referred to as "high-hardness monomer 1");

(VIII) a bifunctional polymerizable monomer (hereinafter, simply referred to as "high-hardness monomer 2").

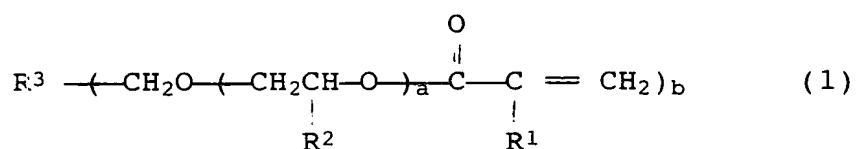
As the polyfunctional polymerizable monomer of the high-hardness monomer 1, known polymerizable monomers can be used without any limitation, provided that it is a polymerizable monomer satisfying the hardness condition for the homopolymer, and having at least three polymerizable groups in the molecule. Desirably, there is used as polymerizable monomer having 3 to 6 polymerizable groups from the standpoint of easy availability on an industrial scale.

Here, the polymerizable group is not particularly limited, provided that it is a group exhibiting the polymerizable properties, but a group exhibiting radically polymerizable properties is desired. The radically polymerizable groups include a methacryloyl group, an acryloyl group, a vinyl group and an allyl group. Among them, a methacryloyl group and an acryloyl group are particularly preferable.

Preferred examples of the high-hardness monomer 1 include trimethacrylate derivative, triacrylate derivative, tetramethacrylate derivative, tetraacrylate derivative,

triisocyanate derivative, tetraisocyanate derivative, triol derivative, trithiol derivative, tetrathiol derivative, triepoxy derivative, triurethane methacrylate derivative, tetraurethane methacrylate derivative, hexaurethane methacrylate derivative, trivinyl derivative, tetravinyl derivative and triallyl derivative. Among them, there can be preferably used trimethacrylate derivative, triacrylate derivative, tetramethacrylate derivative, tetraacrylate derivative, triurethane methacrylate derivative, tetraurethane methacrylate derivative and hexaurethane methacrylate derivative having a methacryloyl group or an acryloyl group.

Among them, it is particularly desired to use a polyfunctional polymerizable monomer represented by the following general formula (1),



wherein R^1 and R^2 are, independently from each other, hydrogen atoms or alkyl groups (i.e., methyl groups or ethyl groups) having 1 to 2 carbon atoms, R^3 is a trivalent to hexavalent organic residue, a is an integer of 0 to 20, and b is an integer of 3 to 6,

from the standpoint of easy availability of the starting

material and easiness for adjusting the hardness of the cured product.

In the above general formula, R^3 is a trivalent to hexavalent organic residue. Concrete examples include a group derived from polyol and an organic group including a trivalent to hexavalent hydrocarbon group or an urethane bond.

Concrete examples of the polyfunctional polymerizable monomer represented by the above general formula (1) that can be favorably used include a trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, tetramethylolmethane trimethacrylate, tetramethylolmethane triacrylate, trimethylolpropane trimethacrylate, tetramethylolmethane tetramethacrylate, tetramethylolmethane tetraacrylate, trimethylolpropanetriethylene glycol trimethacrylate, trimethylolpropanetriethylene glycol triacrylate, ethoxylated pentaerythritol tetraacrylate, ethoxylated pentaerythritol tetramethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, triurethaneoligomer tetraacrylate and urethaneoligomer hexamethacrylate. These polyfunctional polymerizable monomers may be used being mixed together in two or more kinds.

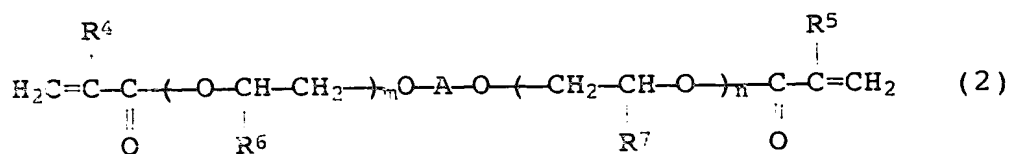
As the bifunctional polymerizable monomer, being the

above-described high-hardness monomer 2, known polymerizable monomers can be used without any limitation, provided that it is a polymerizable monomer satisfying the hardness condition for the homopolymer, and having two polymerizable groups in the molecule. The polymerizable groups are the same as those in the high-hardness monomer 1.

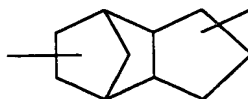
As the bifunctional polymerizable monomer that can be favorably used, there can be exemplified dimethacrylate derivative, diacrylate derivative, divinyl derivative, diallyl derivative, dicyano derivative, diol derivative, dithiol derivative, urethane dimethacrylate derivative, urethane diacrylate derivative, and diepoxy derivative. Among them, there can be exemplified dimethacrylate derivative, diacrylate derivative, urethane dimethacrylate derivative and urethane diacrylate derivative having a methacryloyl group or an acryloyl group.

Among them, a bifunctional polymerizable monomer represented by the following general formulas (2) or the following general formula (3) is particularly preferable, from the standpoint of easy availability of the starting materials and easily adjusting the hardness:

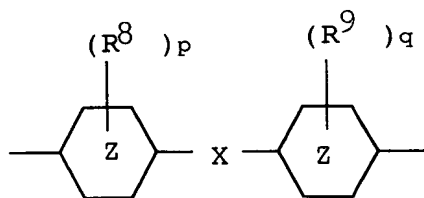
a bifunctional polymerizable monomer represented by:



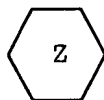
wherein R⁴ and R⁵ are, independently from each other, hydrogen atoms or methyl groups, R⁶ and R⁷ are, independently from each other, hydrogen atoms or alkyl groups having 1 to 2 carbon atoms, A is a straight-chain or branched-chain alkylene group, a substituted or unsubstituted phenylene group, a group represented by the following formula,



or a group represented by the following formula,



wherein R⁸ and R⁹ are, independently from each other, alkyl groups having 1 to 4 carbon atoms, chlorine atoms or bromine atoms, p and q are, independently from each other, integers of 0 to 4, a ring represented by the following formula

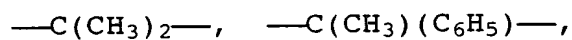
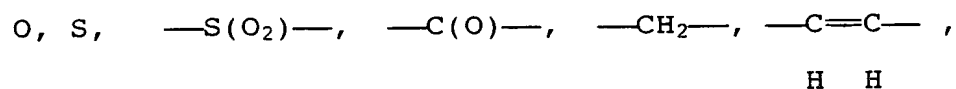


is a benzene ring or a cyclohexane ring, and when the

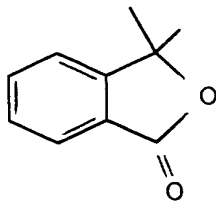
ring represented by the following formula



is a benzene ring, X is any one of the groups represented by the following formulas



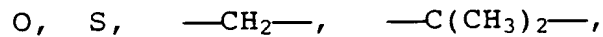
or a group represented by the formula



and when the ring represented by the following formula

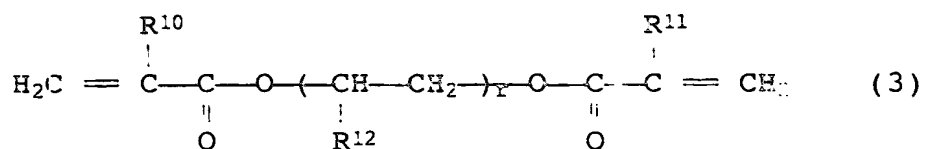


is a cyclohexane ring, X is any one of the groups represented by the following formulas



and m and n are an integer, respectively, and
 m + n is 2 to 6 in average;

or a bifunctional polymerizable monomer represented by:



wherein R¹⁰ and R¹¹ are, independently from each other, hydrogen atoms or methyl groups, R¹² is a hydrogen atom or an alkyl group having 1 to 2 carbon atoms, and r is an integer of 1 to 10.

The bifunctional polymerizable monomer represented by the above general formula (2) is usually obtained in the form of a mixture of molecules having different m and n. In the above formula, therefore, m and n represent values of m+n in average.

Concrete examples of the bifunctional polymerizable monomer include ethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, tripropylene glycol dimethacrylate, tetrapropylene glycol dimethacrylate, nonaethylene glycol dimethacrylate, nonapropylene glycol dimethacrylate, ethylene glycol bisglycidyl methacrylate, bisphenol A dimethacrylate, 2,2-bis(4-methacryloyloxyethoxyphenyl)propane, 2,2-bis(3,5-dibromo-4-methacryloyloxyethoxyphenyl)propane, 1,4-butylene glycol ethylenedimethacrylate, 1,9-nonylene glycol dimethacrylate, neopentylene glycol dimethacrylate, and bis(2-

methacryloyloxyethylthioethyl) sulfide. These bifunctional polymerizable monomers may be used in a mixture of two or more kinds.

The content of the low-hardness monomer and the high-hardness monomer in the curable composition of the present invention is not particularly limited. However, it is desired that the low-hardness monomers are used in amounts of from 1 to 50% by weight and, particularly, from 2 to 30% by weight, and the high-hardness monomers are used in amounts of from 50 to 99% by weight and, particularly, from 70 to 98% by weight based on the total weight of the monomers, so that the cured product thereof exhibits favorable photochromic properties and base member characteristics.

Moreover, from the standpoint of easy moldability of the cured product, with regard to the high-hardness monomer, it is desired to use the high-hardness monomer 1 and the high-hardness monomer 2, and the ratio thereof at that time is preferably such that the high-hardness monomer 1 is used in an amount of from 2 to 50% by weight and, particularly, from 5 to 40% by weight and the high-hardness monomer 2 is used in an amount of from 50 to 98% by weight based on the weight of the whole high-hardness monomers.

Further, the curable composition of the present invention may be blended, as required, with other

polymerizable monomers in addition to the low-hardness monomers and the high-hardness monomers within a range in which they will not impair the effect of the present invention.

Concrete examples of these other polymerizable monomers (hereinafter also referred to as arbitrary monomers) include polymerizable monofunctional monomers, for example, polyallyl compounds such as diallyl phthalate, diallyl isophthalate, diallyl tartarate, epoxy diallyl succinate, diallyl fumarate, diallyl chlorendate, diallyl hexaphthalate, and allyl diglycol carbonate; polythioacrylic acid ester compounds and polythiomethacrylic acid ester compounds such as 1,2-bis(methacryloylthio)ethane, bis(2-acryloylthioethyl) ether, and 1,4-bis(methacryloylthiomethyl)benzene; unsaturated carboxylic acids such as acrylic acid ester compounds and methacrylic acid ester compounds such as glycidyl acrylate, glycidyl methacrylate, β -methylglycidyl methacrylate, bisphenol A-monoglycidyl ether-methacrylate, 4-glycidyloxy methacrylate, 3-(glycidyl-2-oxyethoxy)-2-hydroxypropyl methacrylate, 3-(glycidyloxy-1-isopropoxy)-2-hydroxypropyl acrylate, 3-glycidyloxy-2-hydroxypropyloxy)-2-hydroxypropyl acrylate, acrylic acids, methacrylic acids and maleic anhydride; acrylic acid ester compounds and methacrylic acid ester compounds such as

methyl acrylate, methyl methacrylate, benzyl methacrylate, phenyl methacrylate and 2-hydroxyethyl methacrylate; fumaric acid ester compounds such as diethyl fumarate and diphenyl fumarate; thioacrylic acid and thiomethacrylic acid ester compounds, such as methyl thioacrylate, benzyl thioacrylate and benzyl thiomethacrylate; and vinyl compounds such as styrene, chlorostyrene, methylstyrene, vinyl naphthalene, α -methylstyrene dimer, bromostyrene, and divinyl benzene.

The above arbitrary monomers can be added in a single kind or being mixed in plural kinds together. The amount of addition is usually not larger than 40 parts by weight and, preferably, not larger than 30 parts by weight per a total amount of 100 parts by weight of the low-hardness monomers and the high-hardness monomers.

As the photochromic compound used in the curable composition of the present invention, any known photochromic compound can be used without limitation. Known examples of the photochromic compound are fulgimide compound, spirooxazine compound and chromene compound. In the present invention, it is allowed to use these photochromic compounds. When a photochromic compound having a molecular weight of not smaller than 540 is used, in particular, favorable photochromic properties are exhibited.

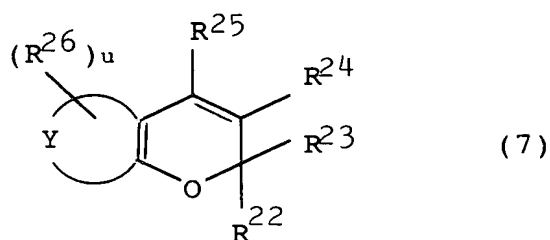
As the fulgimide compound, spirooxazine compound and chromene compound, there can be preferably used those compounds that have been disclosed in, for example, Japanese Unexamined Patent Publication (Kokai) No. 28154/1990, Japanese unexamined Patent Publication (Kokai) No. 288830/1987, PCT International Patent Application No. 22850/1994, and PCI International Patent Application No. 14596/1996.

There can be further favorably used the compounds having excellent photochromic properties that newly discovered by the present inventions and are proposed in pending patent applications (Japanese Patent Applications Nos. 207871/1997, 23110/1999, 27959/1999, 27961/1999, 27960/1999, 140836/1999, 144072/1999, 150690/1999, 144074/1999, 156270/1999, 154272/1999, 188146/1999 and 188902/1999).

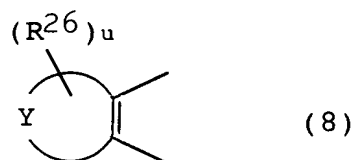
Among these photochromic compounds, a chromene compound exhibits photochromic properties maintaining light resistance larger than that of other photochromic compounds and, further, exhibits particularly greater color density and fading rate among other photochromic properties according to the present invention compared to those of other photochromic compounds, and can be favorably used. Among the chromene compounds, further, the compound having a molecular weight of not smaller than 540 exhibits

markedly improved color density and fading rate among other photochromic properties according to the present invention compared to those of other chromene compounds, and can be used particularly favorably.

As the chromene compound that can be favorably used in the present invention, there can be exemplified a compound represented by the following general formula (7),

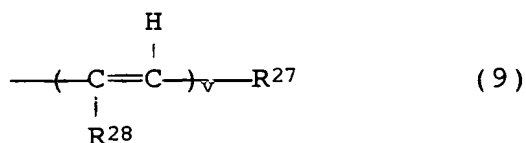


wherein a group represented by the following formula (8)



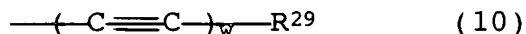
is a substituted or unsubstituted aromatic hydrocarbon group, or a substituted or unsubstituted unsaturated heterocyclic group, R^{24} , R^{25} and R^{26} are hydrogen atoms, alkyl groups, alkoxy groups, aralkoxy groups, amino groups, substituted amino groups, cyano groups, substituted or unsubstituted aryl groups, halogen atoms, aralkyl groups, hydroxy groups, substituted or unsubstituted alkynyl groups,

substituted or unsubstituted heterocyclic groups containing a nitrogen atom as a hetero atom and in which the nitrogen atom is bonded to a pyran ring or to a ring of the group represented by the above formula (7), or condensed heterocyclic groups in which the heterocyclic group is condensed with an aromatic hydrocarbon ring or an aromatic heterocyclic ring, u is an integer of 0 to 6, R²² and R²³ are, independently from each other, groups represented by the following formula (9),



wherein R²⁷ is a substituted or unsubstituted aryl group, or substituted or unsubstituted heteroaryl group, R²⁸ is a hydrogen atom, an alkyl group or a halogen atom, and v is an integer of 1 to 3,

a group represented by the following formula (10),

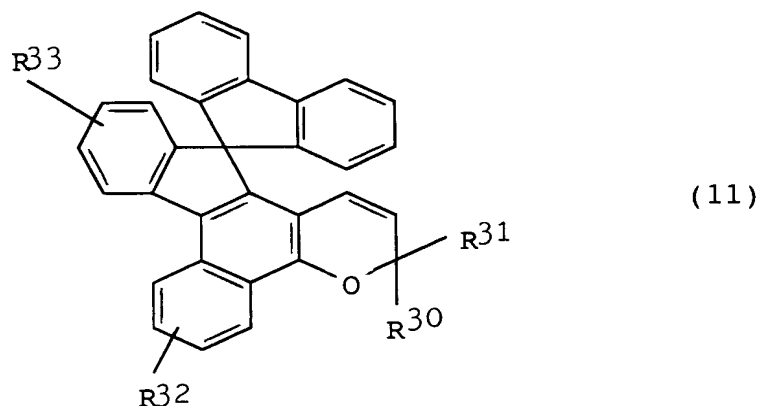


wherein R²⁹ is a substituted or unsubstituted aryl group, or a substituted or unsubstituted heteroaryl group, and w is an integer of 1 to 3, a substituted or unsubstituted aryl group, a substituted or unsubstituted heteroaryl group, or an

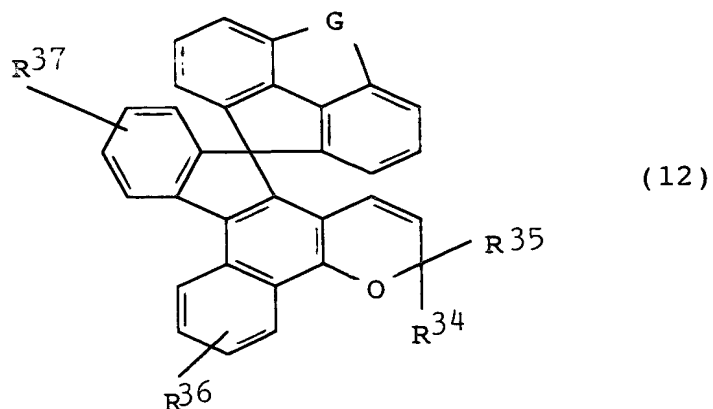
alkyl group, or R^{22} and R^{23} together may constitute an aliphatic hydrocarbon ring or an aromatic hydrocarbon ring.

Further, the substituents defined by R^{24} to R^{26} apply to the substituents in the substituted aryl group or in the substituted heteroaryl group described in the above formulas (9) and (10) and in connection with R^{22} and R^{23} .

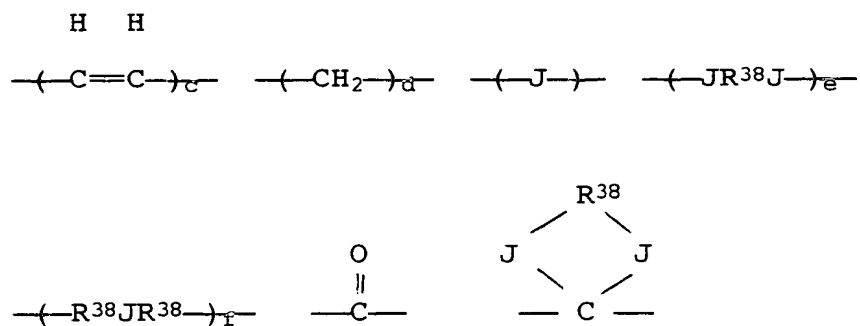
More preferred chromene compounds are those represented by the following general formulas (11) to (16),



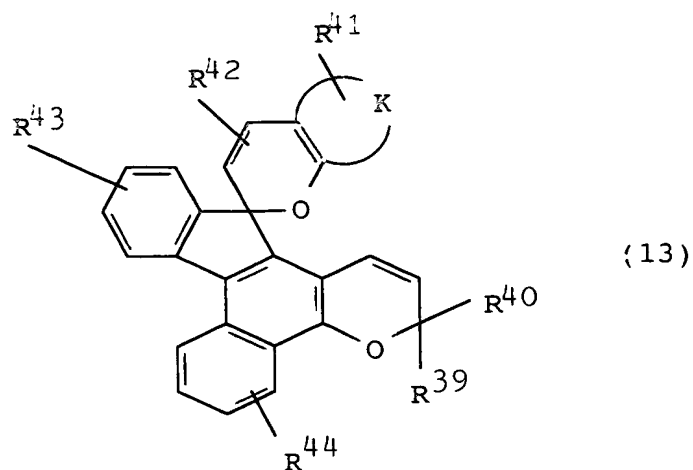
wherein R^{36} and R^{37} are as defined by R^{22} and R^{23} in the above formula (7), R^{32} and R^{33} are as defined by R^{24} , R^{25} and R^{26} in the above formula (7),



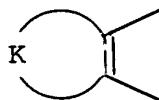
wherein R^{34} and R^{35} are as defined by R^{22} and R^{23} in the above formula (7), R^{36} and R^{37} are as defined by R^{24} , R^{25} and R^{26} in the above formula (7), and G is any one of the groups represented by the following formulas,



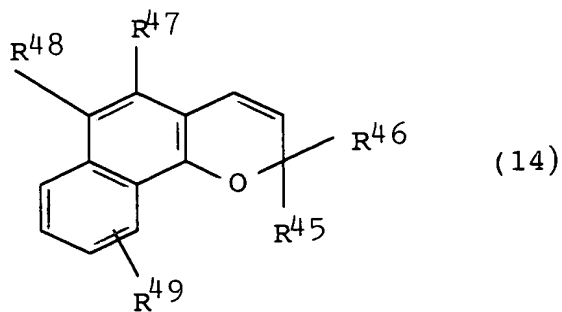
wherein J is an oxygen atom or a sulfur atom, R^{38} is an alkylene group having 1 to 6 carbon atoms, and c , d , e and f are integers of 1 to 4,



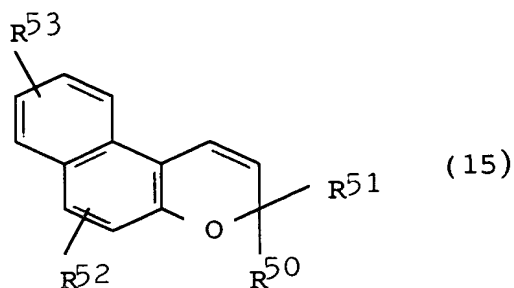
wherein R³⁹ and R⁴⁰ are as defined by R²² and R²³ in the above formula (7), R⁴¹, R⁴², R⁴³ and R⁴⁴ are as defined by R²⁴, R²⁵ and R²⁶ in the above formula (7), and the following formula



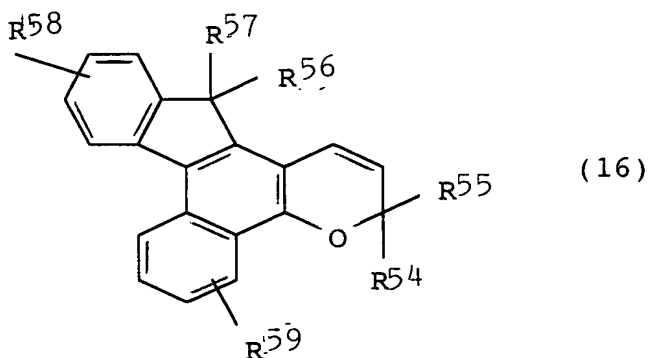
represents a substituted or unsubstituted aromatic hydrocarbon group, or a substituted or unsubstituted unsaturated heterocyclic group,



wherein R⁴⁵ and R⁴⁶ are as defined by R²² and R²³ in the above formula (7), R⁴⁷, R⁴⁸ and R⁴⁹ are as defined by R²⁴, R²⁵ and R²⁶ in the above formula (7),



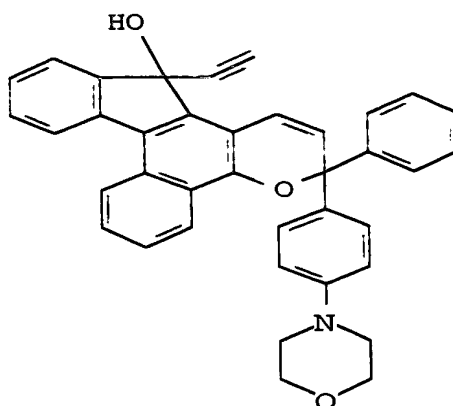
wherein R⁵⁰ and R⁵¹ are as defined by R²² and R²³ in the above formula (7), R⁵², R⁵³ and R⁵⁴ are as defined by R²⁴, R²⁵ and R²⁶ in the above formula (7),



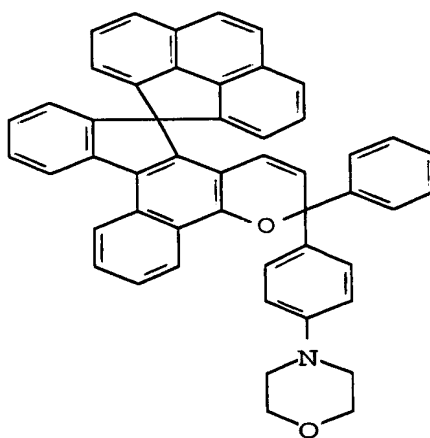
wherein R⁵⁴ and R⁵⁵ are as defined by R²⁸ and R²⁹ in the above formula (7), R⁵⁶, R⁵⁷, R⁵⁸ and R⁵⁹ are as defined by R²⁴ to R²⁶ in the above formula (7).

More preferred chromene compounds of the present invention are those having structures as shown below.

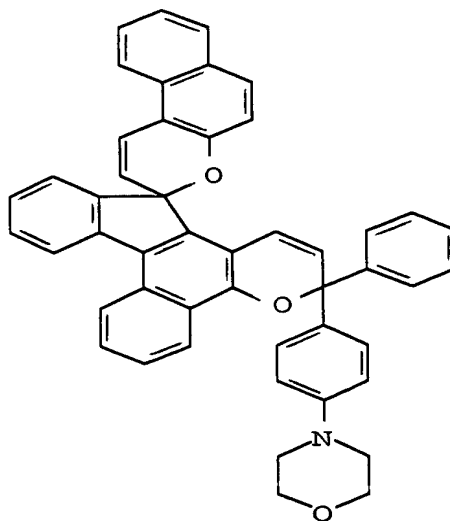
[Chemical F.38]



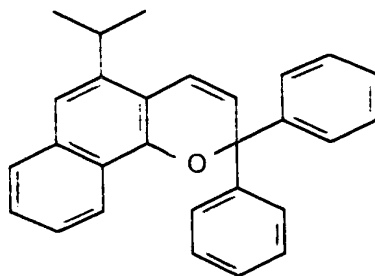
[Chemical F.39]



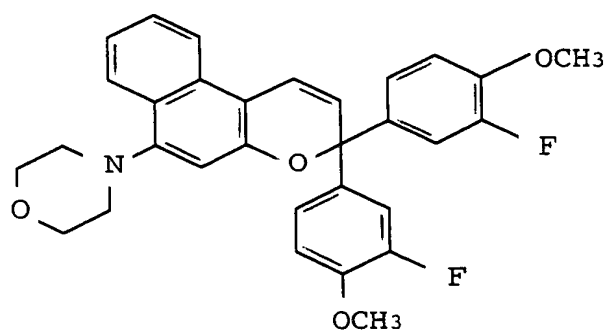
[Chemical F.40]



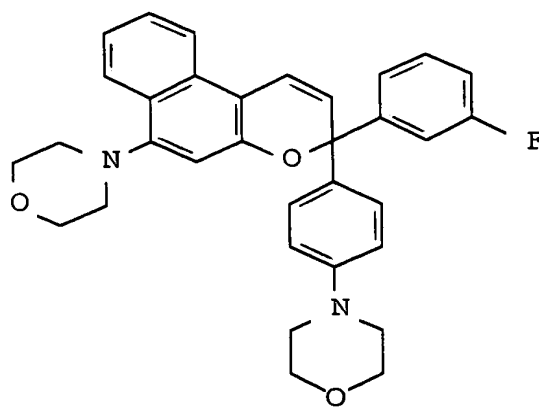
[Chemical F.41]



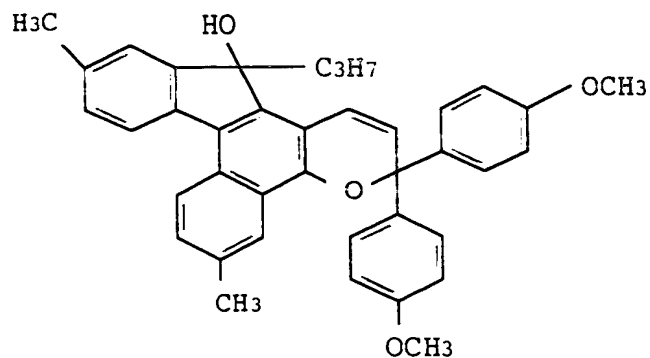
[Chemical F.42]



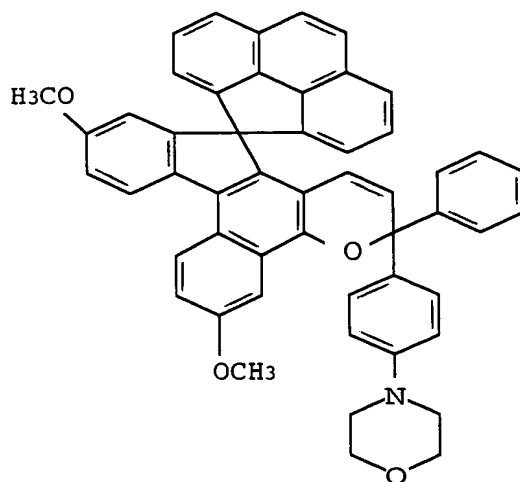
[Chemical F.43]



[Chemical F.44]



[Chemical F.45]



In the curable composition of the present invention, there is no particular limitation on the amount of adding the photochromic compound. Generally, however, the amount of addition is from 0.001 to 5 parts by weight, preferably, from 0.005 to 1 part by weight and, more preferably, from 0.01 to 0.5 parts by weight per 100 parts by weight of all polymerizable monomers inclusive of arbitrary monomers

added as required. When the amount of addition of the photochromic compound is smaller than 0.001 part by weight, the color density may decrease. When the amount of addition is greater than 5 parts by weight, the photochromic compound does not dissolve in the polymerizable monomers to a sufficient degree and becomes nonuniform, often giving rise to the occurrence of shading in the color density.

In order to improve light resistance, color-developing rate and color-fading rate of the photochromic compound, moldability, the curable composition of the present invention may be further blended with additives such as surfactant, antioxidant, radical-trapping agent, ultraviolet stabilizer, ultraviolet absorber, parting agent, coloring-preventing agent, antistatic agent, fluorescent dye, dye, pigment and perfume. Any known additives can be used without limitation.

As the surfactant, for example, there can be used any one of the nonionic type, anionic type or cationic type. From the standpoint of dissolution in the polymerizable monomer, however, it is desired to use a nonionic surfactant. Concrete examples of the nonionic surfactant that can be favorably used include sorbitan fatty acid ester, glycerin fatty acid ester, decaglycerin fatty acid ester, propylene glycol pentaerythritol fatty acid ester,

polyoxyethylenesorbitan fatty acid ester,
polyoxyethylenesorbit fatty acid ester,
polyoxyethyleneglycerin fatty acid ester, polyethylene
glycol fatty acid ester, polyoxyethylenealkyl ether,
polyoxyethylenephytosterol phytostanol,
polyoxyethylenepolyoxypropylenealkyl ether,
polyoxyethylenealkylphenyl ether, polyoxyethylene castor
oil-cured castor oil, polyoxyethylenelanolin-lanolin
alcohol-bee wax derivative, polyoxyethylenealkylamine-fatty
acid amide, polyoxyethylenealkylphenylformaldehyde
condensation product, and single-chain polyoxyethylenealkyl
ether. The surfactants may be used being mixed in two or
more kinds. It is desired that the surfactants are added
in amounts of from 0.1 to 20 parts by weight per 100 parts
by weight of the total polymerizable monomers.

As the antioxidant, radical-trapping agent,
ultraviolet stabilizer and ultraviolet absorber, there can
be preferably used a hindered amine photostabilizer, a
hindered phenol antioxidant, a phenol-type radical-trapping
agent, sulfur-type antioxidant, benzotriazole compound and
benzophenone compound. The antioxidant, radical-trapping
agent, ultraviolet stabilizer and ultraviolet absorber may
be used being mixed in two or more kinds. In using these
nonpolymerizable compounds, there may be further used a
surfactant in combination with the antioxidant, radical-

trapping agent, ultraviolet stabilizer and ultraviolet absorber. It is desired that the antioxidant, radical-trapping agent, ultraviolet stabilizer and ultraviolet absorber are added in amounts over a range of from 0.001 to 1 part by weight per 100 parts by weight of the whole polymerizable monomers.

There is no particular limitation on the method of preparing the curable composition of the present invention; i.e., the composition is prepared by weighing and mixing the components in predetermined amounts. There is no particular limitation on the order of adding the components. All components may be simultaneously added up. Or, the monomer components only may be mixed in advance and, then, for example, the photochromic compound and other additives may be added and mixed just prior to conducting the polymerization as will be described later. In conducting the polymerization as will be described later, a polymerization initiator may further be added as required.

There is no particular limitation on the method of obtaining a photochromic cured product by curing the curable composition of the present invention, and any known polymerization method can be employed depending upon the kinds of the monomers that are used. The polymerization can be initiated by using radical polymerization initiators such as various peroxides and azo compounds, or by being

irradiated with ultraviolet rays, α -rays or γ -rays, or by utilizing both of them.

Though there is no particular limitation on the polymerization method, it is desired to employ the cast polymerization from such a standpoint that the photochromic cured product may be used as a main body of the optical material such as of photochromic lenses. The representative cast polymerization will be described below in further detail.

In this method, the curable composition of the present invention to which a radical polymerization initiator is added, is poured into the mold that is held by an elastomer gasket or a spacer, and is heated in an air furnace so as to be polymerized and cured and is, then, taken out.

There is no particular limitation on the radical polymerization initiator, and any known compound can be used. Representative examples include diacyl peroxides such as benzoyl peroxide, p-chlorobenzoyl peroxide, decanoyl peroxide, lauroyl peroxide and acetyl peroxide; peroxy esters such as t-butylperoxy-2-ethyl hexanoate, t-butylperoxy dicarbonate, cumylperoxy neodecanate, and t-butylperoxy benzoate; percarbonates such as diisopropylperoxy dicarbonate, di-2-ethylhexylperoxy dicarbonate, and di-sec-butyloxy carbonate; and azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-

azobis(4-dimethylvaleronitrile), 2,2'-azobis(2-methylbutylonitrile), and 1,1'-azobis(cyclohexane-1-carbonitrile).

The amount of the radical polymerization initiator varies depending upon the polymerization conditions, kind of the initiator, kind and composition of the curable composition of the present invention, and cannot be exclusively specified. Generally, however, the radical polymerization initiator is used in an amount of from 0.01 to 10 parts by weight per 100 parts by weight of the whole polymerizable monomers.

Among the polymerization conditions, the temperature particularly affects the property of the obtained resin. The temperature varies depending upon the kind and amount of the initiator and the kind of the monomer, and cannot be exclusively specified. Generally, however, it is desired to conduct the so-called tapered two-stage polymerization in which polymerization is started generally at a relatively low temperature, and the temperature is gradually increased to thereby effect curing at a high temperature the curing is effected by raising the temperature from a relatively low temperature, up to a high temperature, preferably, 70 to 120°C at the time when the polymerization is finished.

The polymerization time, too, varies depending upon

various factors like the temperature, and it is desired to determine an optimum time in advance depending upon the conditions. Generally, it is desired to so select the conditions that the polymerization is completed in 2 to 40 hours.

The cast polymerization can be similarly conducted even by the known photo polymerization by using ultraviolet rays. As the photo polymerization initiator in this case, there can be used benzoin, benzoinmethyl ether, benzoinbutyl ether, benzophenol, acetophenone-4,4'-dichlorobenzophenone, diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropane-1-on, benzylmethylketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropane-1-on, 1-hydroxycyclohexylphenyl ketone, and 2-isopropylthioxanthone. In general, these photo polymerization initiators are used in an amount of from 0.001 to 5 parts by weight per 100 parts by weight of the whole monomers.

The cured product of the present invention obtained by the above-mentioned method can be processed in a manner as described below depending upon the applications. That is, the cured product is dyed by using a dye such as dispersion dye, is treated with a hard coating by using a silane coupling agent, a hard coating agent comprising chiefly a sol of an oxide of silicon, zirconium, antimony or

aluminum, or a hard coating agent comprising chiefly an organic high molecules, is subjected to the anti-reflection treatment by being deposited with a thin film of a metal oxide such as SiO_2 , TiO_2 or ZrO_2 or by being coated with a thin film of organic high molecules, or is subjected to the antistatic treatment and a secondary treatment.

(Examples)

The present invention will be described in further detail to which only, however, the invention is in no way limited.

The compounds used in the following Examples are as described below.

(1) Low-hardness monomers.

The L-scale Rockwell hardness of the cured product obtained by homopolymerization may be hereinafter abbreviated simply as "homo-HL" (measuring method is described in Photochromatic Characteristics ④ appearing later.

9PG: Nonapropylene glycol dimethacrylate (homo-HL < 20)

MAPEG (526): Polyethylene glycol methacrylate having an average molecular weight of 526. (homo-HL < 20).

DMAPEG(875): Polyethylene glycol dimethacrylate having an average molecular weight of 875 (homo-HL < 20).

MAPPG (430): Propylene glycol methacrylate having an average molecular weight of 430 (homo-HL < 20).

C18MA: Stearyl methacrylate (homo-HL < 30).

MAMePEG (468): Methyl ether polyethylene glycol methacrylate having an average molecular weight of 468 (homo-HL < 20).

MAMePEG (1100): Methyl ether polyethylene glycol methacrylate having an average molecular weight of 1100 (homo-HL < 20).

MATHF (650): Polyhexamethylene glycol dimethacrylate having an average molecular weight of 650 (homo-HL < 20).

NerolMA: Nerol methacrylate (homo-HL < 20).

OleylMA: Oleyl methacrylate (homo-HL < 20).

MAPhPEG (2034): Octylphenyl ether polyethylene glycol methacrylate having an average molecular weight of 2034 (homo-HL < 20).

SAL9E: Isononyl ether polyethylene glycol methacrylate having an average molecular weight of 608 (homo-HL < 20).

CFMA: Perfluoroheptylethylene glycol methacrylate (homo-HL < 30).

High-hardness monomers.

High-hardness monomers 1.

TMPT: Trimethylolpropane trimethacrylate (homo-HL = 122).

ATM4E: Ethoxylated pentaerythritol tetraacrylate (homo-HL = 100).

TMM360: Pentaerythritol trimethacrylate/pentaerythritol tetramethacrylate = 60/40 (homo-HL = 122).

U4HA: Urethane oligomer tetramethacrylate (homo-HL = 110).

4G: Tetraethylene glycol dimethacrylate (homo-HL = 90).

3G: Triethylene glycol dimethacrylate (homo-HL = 110).

9G: Nonaethylene glycol dimethacrylate (homo-HL < 30)

BPE: 2,2-Bis(4-methacryloyloxyethoxyphenyl)propane (homo-HL = 110).

4PG: Tetrapropylene glycol dimethacrylate (homo-HL = 70).

(3) Arbitrary monomers.

GMA: Glycidyl methacrylate (homo-HL = 80).

α MS: α -Methylstyrene (homo-HL < 40).

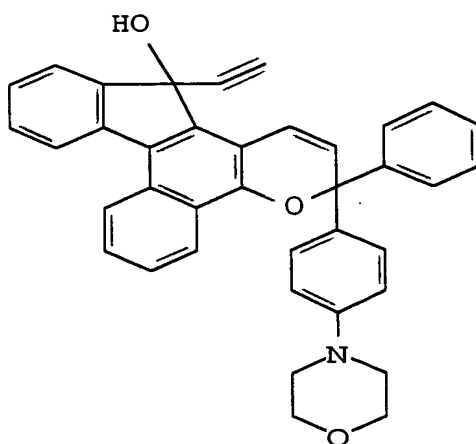
MSD: α -Methylstyrene (not homopolymerized).

HEMA: Hydroxyethyl methacrylate (homo-HL = 80).

(4) Photochromic compounds.

Chromene 1.

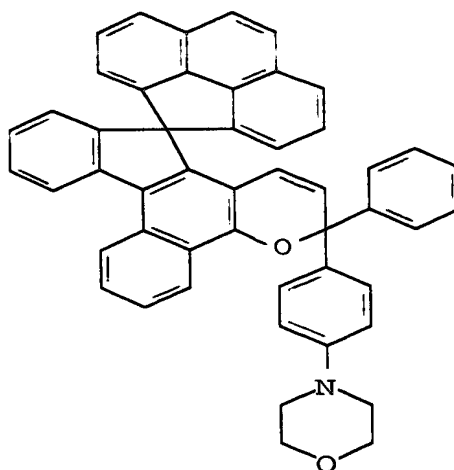
[Chemical F.46]



(molecular weight, 547)

Chromene 2.

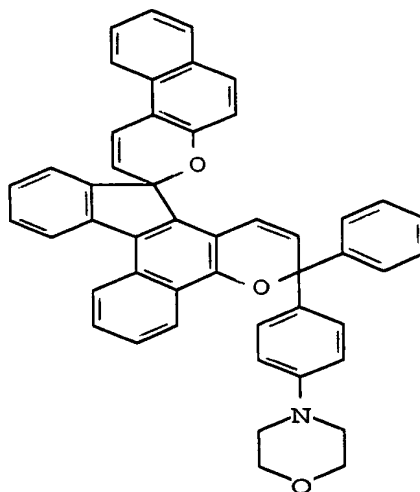
[Chemical F.47]



(molecular weight, 681)

Chromene 3.

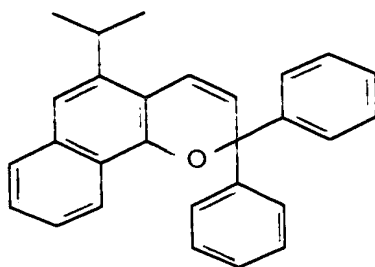
[Chemical F.48]



(molecular weight, 673)

Chromene 4.

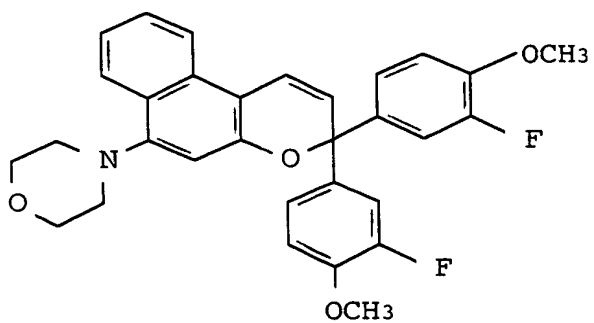
[Chemical F.49]



(molecular weight, 376)

Chromene 5.

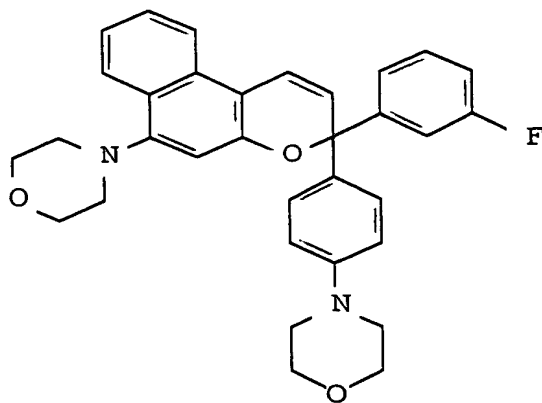
[Chemical F.50]



(molecular weight, 515)

Chromene 6.

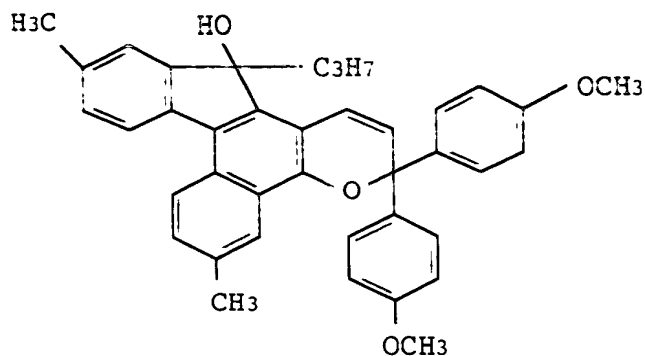
[Chemical F.51]



(molecular weight, 522)

Chromene 7.

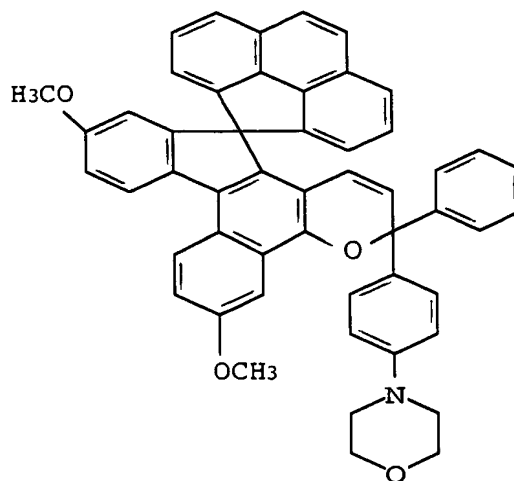
[Chemical F.52]



(molecular weight, 568)

Chromene 8.

[Chemical F.53]



(molecular weight, 741)

(5) Surfactant.

Tween 20: Polyoxyethylene (20) sorbitan monolaurate.

(6) Polymerization initiator.

Perbutyl ND: t-Butylperoxy neodecanate (trade name:

Perbutyl ND, produced by Nippon Yushi Co.).

(Example 1)

0.03 Parts by weight of the chromene 1 and 1 part by weight of the perbutyl ND as the polymerization initiator, were added to 100 parts by weight of polymerizable monomers comprising 20 parts by weight of TMPT, 55 parts by weight of tetraethylene glycol dimethacrylate, 7 parts by weight of glycidyl methacrylate, 5 parts by weight of α MS, 1 part by weight of MSD and 12 parts by weight of MAPEG 526, and were mixed to a sufficient degree. This mixture solution was poured into a mold constituted by a glass plate and a gasket of an ethylene/vinyl acetate copolymer, and was polymerized by cast polymerization. The polymerization was conducted by using an air furnace while gradually raising the temperature from 30°C to 90°C over a period of 18 hours and maintaining the temperature at 90°C for 2 hours. After the polymerization has been finished, the polymer was removed from the glass mold.

The thus obtained polymer sample (2 mm thick) was irradiated with light by using a xenon lamp L-2480 (300W) SHL-100 manufactured by Hamamatsu Photonics Co. through an aeromass filter (manufactured by Coning Co.) at 20°C \pm 1°C at beam intensities on the polymer surface of 365 nm = 2.4 mW/cm² and 245 nm = 24 μ W/cm² for 120 seconds to develop color and to measure the photochromic properties. The

photochromic properties were evaluated by the following methods, and were as shown in Table 1.

- ① Maximum absorption wavelength (λ_{max}): A maximum absorption wavelength after the development of color as found by using a spectrophotometer (instantaneous multi-channel photodetector MCPD 1000) manufactured by Otsuka Denshi Co. The maximum absorption wavelength is related to the color tone at the time when the color is developed.
- ② Color density $\{\epsilon(120) - \epsilon(0)\}$: A difference between an absorbancy $\{\epsilon(120)\}$ after irradiated with light for 120 seconds at the maximum absorption wavelength and $\epsilon(0)$. It can be said that the higher this value, the more excellent the photochromic properties are.
- ③ Fading rate $[t_{1/2} \text{ (min)}]$: The time until the absorbancy of a sample at the maximum wavelength drops down to one-half the $\{\epsilon(120) - \epsilon(0)\}$ from when the sample is no longer irradiated with light after it was irradiated with light for 120 seconds. It can be said that the shorter the time, the more excellent the photochromic properties are.
Moreover, the properties of the base members were evaluated by the following items:
- ④ L-scale Rockwell hardness (HL): After left to stand in a room maintained at 25°C for one day, the cured product was measured for its L-scale Rockwell hardness by using the Akashi Rockwell hardness meter (model, AR-10).

⑤ Impact resistance: A steel ball was permitted to naturally fall on a test plate having a thickness of 2 mm and a diameter of 65 mm from a height of 127 cm, and the impact resistance was evaluated in terms of the weight of the steel ball by which the test plate was broken. The basis of evaluation was such that "1" was when the weight of the steel ball at this moment was smaller than 20 g, "2" was when the weight was 20 to 40 g, "3" was when the weight was 40 to 60 g, "4" was when the weight was 60 to 80 g, and "5" was when the weight was not smaller than 80 g.

⑥ Heat resistance: The molded and cured product was fitted to the frame and was heated at 120°C. ○ represents the case when the frame was not deviated, and × represents the case when the frame was deviated.

(Examples 2 to 42)

Photochromic cured products were obtained in the same manner as in Example 1 but using polymerizable monomer compositions, chromene compounds and other additives shown in Tables 1 to 3, and were evaluated for their photochromic properties. The results were as shown in Tables 1 to 3.

(Comparative Examples 1 to 10)

Moreover, for comparison sake, photochromic cured products were obtained in the same manner as in Example 1, except that the polymerizable monomer composition and chromene compounds as shown in Table 4 were used, and the

photochromic properties were evaluated. The evaluation results are shown in Table 4.

Table 1

Ex. No.	Low-hardness monomer (parts by wt.)	High-hardness monomer (parts by wt.)	Arbitrary monomer (parts by wt.)	Other additives (parts)	Chromene compound (parts)
1	MAPEG(526) 5	TMPT/4G 5/77	GMA/ α MS/MSD 7/5/1	—	chromene 1 0.03
2	MAPEG(526) 10	TMPT/4G 20/57	GMA/ α MS/MSD 7/5/1	—	chromene 1 0.03
3	MAPEG(526) 20	TMPT/4G 40/27	GMA/ α MS/MSD 7/6/1	—	chromene 1 0.03
4	MAPEG(526) 10	TMPT/U4HA/4G 20/10/47	GMA/ α MS/MSD 7/5/1	—	chromene 1 0.03
5	MAPPG(430) 5	TMPT/4PG 10/85	—	—	chromene 1 0.03
6	MAPPG(430) 10	TMPT/4PG 25/65	—	—	chromene 1 0.03
7	MAPPG(430) 20	TMPT/4PG 40/40	—	—	chromene 1 0.03
8	MAPPG(430) 10	TMPT/U4HA/4G 20/13/57	—	—	chromene 1 0.03
9	C18MA 10	TMPT/BPE/3G 20/35/20	GMA/ α MS/MSD 9/5/1	—	chromene 2 0.03
10	MAPPG(430) 15	TMPT/BPE/4PG 20/20/30	GMA 15	—	chromene 2 0.03
11	MAPEG(526)/ MAPPG(430) 5/5	TMPT/U4HA/BPE/4PG 20/10/45	GMA/MSD 14/1	—	chromene 2 0.03
12	DMAPEG(875) 20	TMPT/4G/3G 20/45/12	GMA 15	—	chromene 2 0.03
13	MAPEG(526) 12	ATM4E/4G 48/40	—	—	chromene 3 0.03
14	MAPPG(430) 10	TMPT/4PG 20/55	α MS 15	—	chromene 3 0.05
15	MAPPG(430) 15	TMPT/BPE/4PG 20/35/28	MSD 2	—	chromene 4 0.05
16	MAPEG(526) 10	TMPT/4G 20/57	GMA 15	—	chromene 5 0.05
17	9PG 30	TMPT/4G/3G 30/20/5	GMA 15	—	chromene 5 0.05
18	MAPEG(526) 15	TMPT/ATM4E/4PG 20/35/30	—	—	chromene 6 0.03
19	DMAPEG(875) 20	TMPT/4G/3G 20/45/12	GMA 13	—	chromene 7 0.03
20	DMAPEG(875) 20	TMPT/4G/3G 20/45/12	GMA 13	Tween20 0.5	chromene 7 0.03
21	MAPEG(468) 10	TMPT/4G/3G 20/48/15	GMA/ α MS/MSD 7/5/1	—	chromene 8 0.03

Table 1 (continued)

<u>Ex.No.</u>	<u>λ_{Max} (nm)</u>	<u>Color density</u>	<u>Fading rate</u> <u>(min)</u>	<u>HL</u> <u>hardness</u>	<u>Heat</u> <u>resistance</u>	<u>Impact</u> <u>resistance</u>
1	586	0.8	2	88	○	4
2	586	1.1	1	96	○	4
3	586	1.3	0.6	100	○	3
4	586	0.9	1	94	○	5
5	584	0.9	1.5	86	○	3
6	584	1.2	0.8	93	○	3
7	584	1.4	0.5	100	○	3
8	584	1	0.9	95	○	4
9	580	0.72	0.6	94	○	4
10	580	0.8	0.5	96	○	4
11	580	0.82	0.5	95	○	5
12	580	0.9	1.1	95	○	4
13	580	1	1.5	90	○	3
14	580	1	1.8	93	○	4
15	478	1.5	2.5	96	○	4
16	442	1.2	1.1	96	○	3
17	442	1.1	1.3	100	○	3
18	478	1.2	1	88	○	3
19	576	0.8	2.5	92	○	3
20	576	0.9	2	91	○	3
21	610	0.73	0.9	98	○	4

Table 2

Ex. No.	Low-hardness monomer (parts by wt)	High-hardness monomer (parts by wt)	Arbitrary monomer (parts by wt)	Other additives (parts)	Chromene compound (parts)
22	MAMEPEG(468) 10	TMPT/4G/3PG 20/15/45	GMA/MSD 10/1	—	chromene 8 0.03
23	MAMEPEG(468) 10	TMPT/4G/3PG 15/5/58	GMA/αMS/MSD 10/2/1	—	chromene 8 0.03
24	MAMEPEG(468) 10	TMPT/BPE/3G 20/48/5	GMA/αMS/MSD 9/8/1	—	chromene 8 0.03
25	MAMEPEG(468) 10	TMPT/BPE/9G 20/48/5	GMA/HEMA/αMS/MSD 4/5/8/1	—	chromene 8 0.03
26	MATHF(650) 10	TMPT/4G 10/67	GMA/αMS/MSD 7/5/1	—	chromene 1 0.03
27	NerolMA 5	TMPT/4G 20/59	GMA/αMS/MSD 7/5/1	—	chromene 1 0.03
28	OleylMA 5	TMPT/4G 20/59	GMA/αMS/MSD 7/5/1	—	chromene 1 0.03
29	PhMAPEG(2034) 3	TMPT/4G 20/59	GMA/αMS/MSD 7/5/1	—	chromene 1 0.03
30	SAL9E 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 1 0.03
31	MAMEPEG(1100) 10	TMM360/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 1 0.03
32	CFMA 10	TMM360/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 1 0.03
33	MAMEPEG(468) 15	TMM360/BPE 20/48	GMA/αMS/MSD 9/8/1	—	chromene 1 0.03
34	PhMAPEG(2034) 5	TMPT/BPE/4G 20/48/10	GMA/αMS/MSD 9/8/1	—	chromene 1 0.03
35	MAMEPEG(468) 10	TMPT/4PG/3PG 20/15/30	GMA/MSD 10/1	—	chromene 1 0.03
36	MAPEG(526) 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 2 0.03
37	MAPEG(526) 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 3 0.03
38	MAPEG(526) 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 4 0.03
39	MAPEG(526) 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 5 0.03
40	MAPEG(526) 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 6 0.03

Table 2 (continued)

<u>Ex.No.</u>	<u>λ Max (nm)</u>	<u>Color density</u>	<u>Fading rate</u> <u>(min)</u>	<u>HL</u> <u>hardness</u>	<u>Heat</u> <u>resistance</u>	<u>Impact</u> <u>resistance</u>
22	606	0.88	0.85	98	○	4
23	606	0.91	0.88	100	○	3
24	614	0.68	1	88	○	4
25	614	0.72	0.9	84	○	4
26	584	0.7	0.96	88	○	4
27	584	0.7	0.85	93	○	4
28	584	0.7	1.1	90	○	3
29	584	0.68	0.67	84	○	4
30	584	0.8	1	98	○	4
31	584	0.75	0.82	92	○	3
32	584	0.7	0.85	89	○	3
33	592	0.8	0.8	82	○	3
34	584	0.7	0.62	86	○	4
35	584	0.8	1	90	○	4
36	580	0.7	0.7	96	○	4
37	580	1	1.3	96	○	4
38	478	1.2	3.8	96	○	4
39	442	1.1	1.5	96	○	4
40	478	0.95	1.4	96	○	4

Table 3

Ex. No.	Low-hardness monomer (parts by wt)	High-hardness monomer (parts by wt)	Arbitrary monomer (parts by wt)	Other additives (parts)	Chromene compound (parts)
41	MAPEG(526) 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 7 0.03
42	MAPEG(526) 10	TMPT/4G 20/57	GMA/αMS/MSD 7/5/1	—	chromene 8 0.03

Table 3 (continued)

Ex. No.	λ _{Max} (nm)	Color density	Fading rate (min)	HL hardness	Heat resistance	Impact resistance
42	574	0.8	1.2	96	○	4
43	586	0.75	0.9	96	○	4

Table 4

<u>Comp. Ex. No.</u>	<u>Low-hardness monomer (parts by wt)</u>	<u>High-hardness monomer (parts by wt)</u>	<u>Arbitrary monomer (parts by wt)</u>	<u>Other additives (parts)</u>	<u>Chromene compound (parts)</u>
1	—	4G 85	GMA/αMS/MSD 9/5/1	—	chromene 1 0.03
2	—	TMPT 85	GMA/αMS/MSD 9/5/1	—	chromene 1 0.03
3	MAPEG(526) 85	—	GMA 15	—	chromene 1 0.03
4	—	4G 85	GMA/αMS/MSD 9/5/1	—	chromene 2 0.05
5	—	4G 85	GMA 15	—	chromene 3 0.05
6	—	4G 85	GMA 15	—	chromene 4 0.05
7	—	4G 85	GMA 15	—	chromene 5 0.03
8	—	4G 85	GMA 15	—	chromene 6 0.03
9	—	4G 85	GMA 15	—	chromene 7 0.03
10	—	4G 85	GMA 15	—	chromene 8 0.03

Table 4 (continued)

<u>Ex.No.</u>	<u>λ Max (nm)</u>	<u>Color density</u>	<u>Fading rate</u> <u>(min)</u>	<u>HL</u> <u>hardness</u>	<u>Heat</u> <u>resistance</u>	<u>Impact</u> <u>resistance</u>
1	584	0.5	4.6	95	○	5
2	582	0.9	1.5	120	×	1
3	584	1.1	1	<10	×	5
4	584	0.3	2	95	○	5
5	584	0.4	4	95	○	5
6	478	1	6	95	○	5
7	442	1	3	95	○	5
8	478	1	3	95	○	5
9	574	0.3	5.5	95	○	5
10	610	0.4	6	95	○	5

As described above, the base member obtained from a polymerizable monomer having HL of not higher than 40 exhibits excellent photochromic properties but is not practicable because of its low heat resistance. The matrix obtained from a polymerizable monomer having HL of not smaller than 60 exhibits practicable substrate characteristics but insufficient photochromic properties. Both properties, i.e., photochromic properties and matrix properties, are satisfied by using a polymerizable monomer having HL of not higher than 40, a polymerizable monomer having HL of not smaller than 60 in combination. Photochromic cured products of Examples 1 to 42 of the present invention exhibit well-balanced photochromic properties such as color density, fading rate and hardness, as well as impact resistance and heat resistance which are properties of the base member.

(Effects of the Invention)

The photochromic cured product of the present invention exhibits excellent photochromic properties such as a high color density and a large fading rate, and exhibits excellent base member properties such as a high hardness, a high heat resistance and a high impact resistance.

Therefore, the cured product obtained from the photochromic composition of the present invention is very

useful as an optical material such as a photochromic lens material.

(Document Name) ABSTRACT

(Summary)

(Purpose) To provide a photochromic cured product having high color density, large fading rate and exhibiting excellent photochromic properties, and further exhibiting excellent properties of the base member, such as hardness, heat resistance and impact resistance of the cured product.

(Composition) A curable composition contains a polymerizable monomer having the L-scale Rockwell hardness of not larger than 40, a bifunctional or polyfunctional polymerizable monomer having the L-scale Rockwell hardness of not smaller than 60, and a photochromic compound is polymerized and cured.

(Selected Drawing) None